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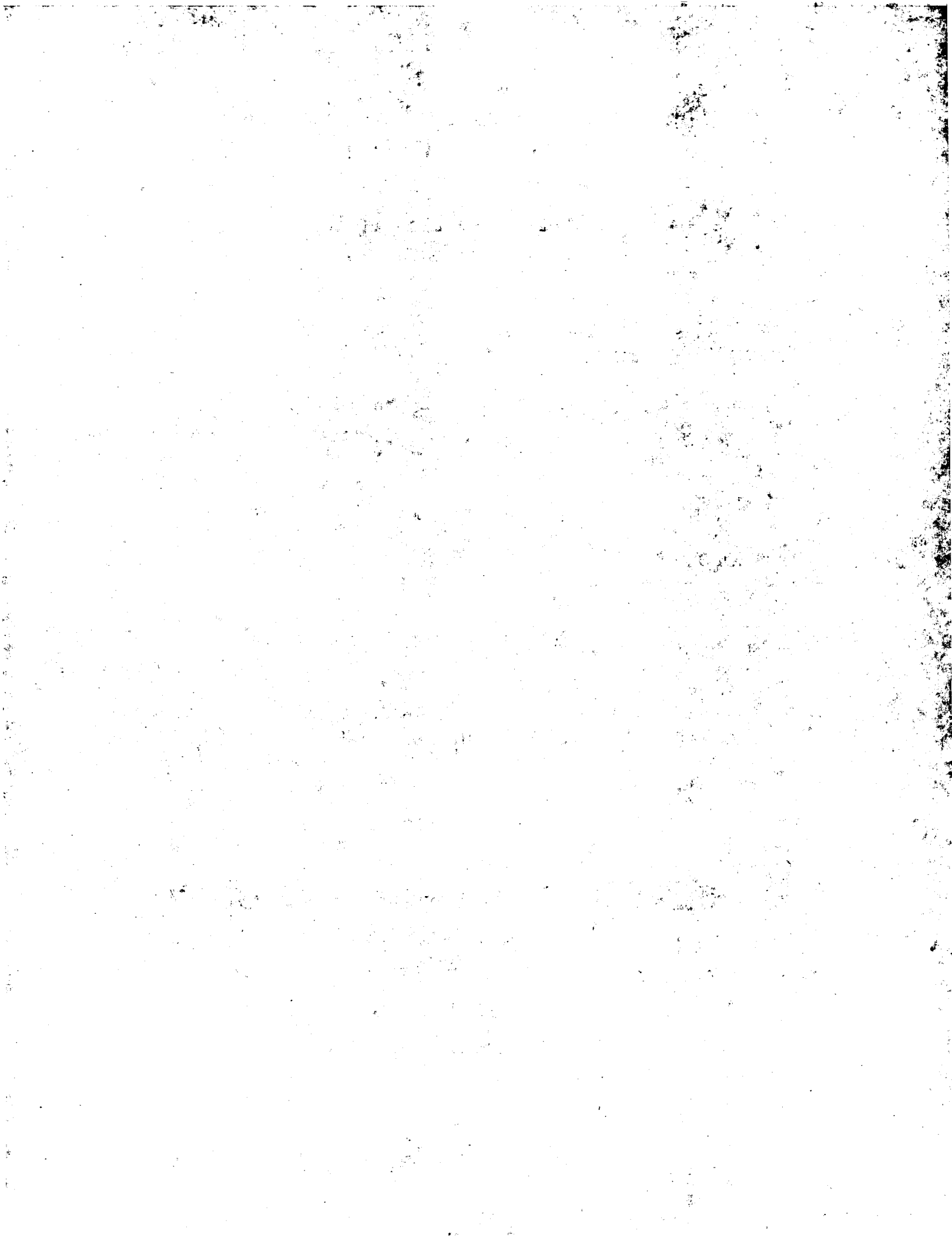
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EP-A- 0 261 820
Dialog Information Services, PAPERCHEM abstract no. 58-06651, Miyamoto, S et al:
"Manufacture of Paper in Neutral Condition",
Jap. Pat. Kokai 110, 998/87 May 22, 1987 9 p.

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Description

A process for the production of paper

5 The present invention relates to a process for the production of paper utilizing an improved retention- and dewatering system. More particularly the invention relates to the use of a combination of a cationic polyacrylamide, a cationic starch and polymeric silicic acid as retention- and dewatering system in the production of paper.

10 It is previously known to use combinations of a cationic polymeric retention agent and an anionic inorganic silica based sol at the production of paper in order to improve retention and dewatering. In the European patent 41056 is for example disclosed a combination of a silica sol and cationic starch. In the PCT application WO 86/05826 is described combinations of silica sols, containing aluminum modified silica particles, and cationic polyacrylamide. In the PCT application WO 86/00100 are disclosed combinations of the same silica sols and cationic starch. Combinations of silica sols and other cationic polymers are also known. The commercial silica
15 based colloids which have been increasingly used in papermaking together with cationic polymeric retention agents during the last few years are of the type which has colloidal particles generally with a particle size of from about 4 nm to about 7 nm, ie a specific surface area of from about 700 to about 300 m²/g, although it is known, eg from the European patent 41056, to use polymeric silicic acid in papermaking. It has generally been considered that colloidal silicic acid sols with particles of above given size give the best results and these have
20 also been preferred with regard to stability. In the Japanese patent application with Early-Disclosure No. 87-110998 it has also been suggested to use colloidal silica with both cationic starch and a cationic or amphoteric polyacrylamide. Also according to this application the colloidal silicic acid should preferably have a surface area of from 300 to 700 m²/g and in all examples a colloidal silica with a specific surface area of 500 or 550 m²/g has been used. The effect of systems comprising an anionic inorganic silica based sol and a cationic component is based on interaction between two substances of different charges and it is supposed that the sol
25 particles with their strong anionic charges to some extent give rise to cross-linking of the polymeric retention agent.

According to the present invention it has been found that a combination of polymeric silicic acid with two cationic polymers, cationic starch and cationic polyacrylamide, gives a surprisingly great improvement of the
30 retention- and dewatering effect at papermaking. This improvement in effect does not originate from the combination of the cationic polymers as such, nor can it be predicted from the effect of the combination of the polymeric silicic acid with the individual cationic polymers. A synergistic effect is obtained when cationic starch and cationic polyacrylamide are used together with the polymeric silicic acid, as is evident from the examples. Thanks to the improved retention and dewatering a greater part of the fine fibers and optional filler is retained
35 in the paper and at the same time the speed of the paper machine can be increased and the energy consumption in the press- and drying sections can be decreased.

The present invention thus relates to a process for the production of paper by forming and dewatering a suspension of cellulose fibers and optional fillers on a wire as stated in the appended claims.

40 The polymeric silicic acid is such which is disclosed in the Swedish patent application 8801951-8, which is hereby incorporated herein by reference. The polymeric silicic acid has a very high specific surface area which at its lowest is 1050 m²/g. The particles suitably have a specific surface area within the range of from 1100 to 1700 m²/g and preferably within the range of from 1200 to 1600 m²/g. The given specific surface area is measured by titration according to the method disclosed by Sears in Analytical Chemistry 28(1956)1981. The polymeric silicic acid can be prepared by acidification of alkali metal silicate, such as potassium or sodium
45 water glass, preferably sodium water glass. These are available with varying molar ratios of SiO₂ to Na₂O or K₂O and the molar ratio is usually within the range of from 1.5:1 to 4.5:1 and the water glass usually has an original pH around 13 or above 13. Any such alkali metal silicate or water glass can be used for the preparation of the fine particle polymeric silicic acids and this preparation is carried out by acidification of a diluted aqueous solution of the silicate. For the acidification mineral acids, such as sulphuric acid, hydrochloric acid and phosphoric acid, or acid ion exchange resins can for example be used. A number of other chemicals for acidification
50 at production of polysilicic acid are also known and some examples of such other chemicals are ammonium sulphate and carbon dioxide. Mineral acids or acid ion exchange resins or combinations of these are suitably used. The acidification is carried out to a pH within the range of from 1 to 9 and suitably to a pH within the range of from 1.5 to 4. The polymeric silicic acid which is termed activated silicic acid, which is prepared by
55 partial neutralization of the alkali metal content to a pH of about 8 to 9 and polymerization usually during about half an hour to an hour, can be used as such directly thereafter but must otherwise be diluted to a content of not more than 1 per cent by weight for interrupting the polymerization or be acidified to the preferred pH range in order to avoid gelation.

The acidification according to the above is most suitably carried out by means of acid ion exchangers, among other things to get more stable products and to avoid that salts from the acidification are added to the stock through the polymeric silicic acid. The polymeric silicic acid which is formed at the acidification consists of macro-molecules or particles of a size of the order of 1 nm which form voluminous chains and networks. Compared with the silica sols of larger particle size which are used commercially in papermaking those which are utilized according to the present invention are considerably less stable both with regard to stability in relation to concentration and stability at storage. The polymeric silicic acids should thus after the acidification suitably not be present in higher concentrations than about 5 per cent by weight, and preferably not higher than 2 per cent by weight. They should not be stored for too long times but it has, nonetheless, been found that a certain storage time can be advantageous. Thus, for example, a storage of a day or a couple of days at a concentration of not more than about 4 to 5 per cent by weight is entirely acceptable with regard to stability and can even result in an improved effect. At a concentration of 1%, or below, storage for two to three weeks without impaired stability is possible and all the time with good effect, or even better effect than without storage. After storage for about three weeks at room temperature an initial gelation is noticeable.

Although the preparation of polymeric silicic acids with high specific surface area by acidification as above described is the preferred method, it is also possible to prepare such polymeric silicic acids which have the high specific surface area and which consist of macromolecules or particles of a size of the order of 1 nm which form voluminous chains and networks by other methods. Such polymeric silicic acids can thus be prepared by polymerization of an alkali metal silicate solution using an initiator such as alum, sodium aluminate and sodium borate.

The polymeric silicic acids which are used according to the present process should thus be produced in connection with their use and such a production at the location in or close to a paper mill is per se advantageous in that cheap raw materials and simple preparation processes are used. The economy of the present process will thus be very good since the polymeric silicic acid is economically advantageous.

Cationic polyacrylamides are per se known as additives in papermaking, primarily to increase retention of fine fibers and fillers, and any cationic polyacrylamide can be used in the present process. The cationic starch can be a for papermaking conventional cationic starch. The starch is made cationic by substitution with ammonium groups in a per se known manner. It is suitable to use a starch with a degree of substitution of at least 0.01.

The amount of polymeric silicic acid which is used depends on the specific stock, the presence of fillers and other conditions at the papermaking. Too small amounts do not give any effect and too great amounts do not give any further improvement of dewatering and retention but only increased costs. The amount of polymeric silicic acid should suitably be at least 0.01 g/kg (kg/ton), calculated as SiO_2 on dry fibers and optional fillers, and is suitably within the range from 0.05 to 5 g/kg (kg/ton). Amounts within the range of from 0.1 to 3 g/kg (kg/ton) are preferred.

The weight ratio between the total amount of the cationic retention agents, ie polyacrylamide and starch, and polymeric silicic acid can vary within wide limits depending on the composition of the stock, the presence of filler etc.. Usually the ratio of polyacrylamide+starch to polymeric silicic acid, calculated as SiO_2 , is above 0.1:1, suitably above 1:1. The upper limit is not critical but is mainly decided from reasons of economy. A weight ratio between (polyacrylamide + starch) and polymeric silicic acid within the range of from 1:1 to 100:1 is preferred.

The weight ratio between cationic starch and cationic polyacrylamide should be within the range of from 0.5:1 to 200:1. The weight ratio is suitably within the range of from 2:1 to 100:1 and preferably from 4:1 to 50:1.

The improvement of the retention and dewatering through the disclosed process is obtained over a pH of the stock of from about 4 to about 10.

The three components can be added to the fiber suspension in arbitrary order. The position for the additions is not critical, but it is preferred not to add the polyacrylamide to the stock in an early stage of the paper production since it is sensitive to the type of mechanical stress which, for example, occurs in mixing apparatus. It is preferred to add the cationic starch to the stock first and then to add the cationic polyacrylamide or the polymeric silicic acid in any order. A particular improvement in comparison with known technique is obtained if the cationic starch is added to the stock first, followed by the cationic polyacrylamide and then the polymeric silicic acid.

The three component system according to the invention can be used for production of paper from different kinds of stocks containing cellulose fibers. The three component system can for example be used for stocks from fibres from chemical pulp, such as sulphate and sulphite pulp, thermo-mechanical pulp, refiner mechanical pulp or groundwood pulp, from as well hardwood as softwood. The system can of course also be used for stocks based on recycled fibres. Particularly good results have been obtained with stocks which are usually considered as difficult, namely both such which contain comparatively high amounts of non-cellulose substance-

es such as lignin and dissolved organic materials, for example different types of mechanical pulps such as groundwood pulp, and such which contain recycled fibers. The combination according to the invention is thus particularly suitable for stocks containing at least 25 per cent by weight of mechanical pulp and/or pulp from recycled fibers, based on the amount of dry pulp. The terms paper and paper production which are used herein do of course include, in addition to paper and paper production, other cellulose fiber containing products in sheet or web form and their preparation, for example pulp sheets, board and paper board.

The present combinations can of course be used in the production of paper in combination with other conventional additives for papermaking such as hydrophobing agents, dry strength agents, wet strength agents etc.. It is particularly suitable to use aluminum compounds in combination with the polymeric silicic acid and the two cationic polymers since it has been found that these can give a further improvement of retention and dewatering. Any for papermaking per se known aluminum compound can used, for example alum, polyaluminum compounds, aluminates, aluminum chloride and aluminum nitrate. The amount of aluminum compound can vary within wide limits and it is suitable to use the aluminum compound, calculated as Al_2O_3 , in a weight ratio to the polymeric silicic acid, calculated as SiO_2 , of at least 0.01:1. The ratio suitably does not exceed 3:1 and is preferably within the range of from 0.02:1 to 1.5:1. The polyaluminum compounds can for example be polyaluminum chlorides, polyaluminum sulfates and polyaluminum compounds containing both chloride and sulfate ions. The polyaluminum compounds can also contain other anions than chloride ions, for example anions from sulfuric acid, phosphoric acid, organic acids such as citric acid and oxalic acid.

The invention is further illustrated in the following examples which, however, are not intended to limit the same. Parts and per cent relate to parts by weight and per cent by weight respectively, unless otherwise stated.

Example 1

In this example the dewatering was evaluated by means of a "Canadian Standard Freeness (CSF) Tester" which is the conventional method for characterizing of dewatering or drainage capability according to SCAN-C 21:65.

In the tests polymeric silicic acid, cationic polyacrylamide and cationic starch were used and the stock was made up from 100% groundwood pulp.

The polymeric silicic acid was prepared from water glass ($\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$) which was diluted with water to an SiO_2 content of 5 per cent by weight. The aqueous solution was ion exchanged with ion exchange resin Amberlite IR-120 to a pH of 2.3. The specific surface area of the obtained acid polymeric silicic acid was measured by titration according to the method given earlier and was found to be $1450 \text{ m}^2/\text{g}$.

To the stock 0.5 g/kg (kg/t) of alum, calculated as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were added. The pH of the stock was 7.8 and its dewatering capability was 170 ml CSF when the stock contained only groundwood pulp and 180 ml when alum had been added. All additions of chemicals were made at a mixing speed of 800 rpm in a "Britt Dynamic Drainage Jar" with a blocked outlet for 45 seconds and the system was then transferred to the Canadian Standard Freeness Tester apparatus. In all test the chemicals were added in the order cationic starch, cationic polyacrylamide and polymeric silicic acid. The additions of chemicals have been calculated in g(kg) per kg(ton) dry stock system (fibers + fillers) and the amounts of polymeric silicic acid, cationic starch and cationic polyacrylamide are given as dry substance.

Test	Cationic starch	Polyacryl- amide	Polymeric silicic acid	CSF
No	g/kg(kc/t)	g/kg(kg/t)	g/kg(kg/t)	ml
1	-	-	1.0	175
2	6	-	-	250
3	-	0.3	-	265
4	6	0.3	-	300
5	6	-	1.0	355
6	-	0.3	1.0	330
7	6	0.3	1.0	520
8	6	0.3	0.5	465
9	6	0.2	1.0	490
10	4	0.2	1.0	475

Test 7 shows the clearly improved dewatering when using a combination of polymeric silicic acid, cationic polyacrylamide and cationic starch. Even when the addition of polymeric silicic acid is reduced the effect is clearly better than when only two of the components are used, as evident from test 8. Tests 9 and 10 show that also the addition of polyacrylamide and starch can be reduced without any drastic reduction of the positive effect.

Example 2

In order to evaluate the addition of chemicals on retention of fillers and fine fibers a "Britt Dynamic Drainage Jar" was used, which is the conventional method for evaluation of retention in paper industry. The agitation speed was 800 rpm.

The stock was composed of 60% bleached birch sulphate and 40% bleached pine sulphate. 30% of chalk were added to the stock as filler. 1 g/l of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was added. The concentration of the stock was 5 g/l and the pH was 7.5. The fines fraction was 30.3%.

The polymeric silicic acid was a polymeric silicic acid prepared from water glass using ion exchange resin for preparation of an acid sol that had been stored for a day and night as a 5% solution and then diluted to a concentration of 1% and then further stored for 3 days and nights before use. The specific surface area for the polymeric silicic acid was 1500 m^2/g . The chemicals were added in the order starch, polyacrylamide and polymeric silicic acid. A comparison was also made with a commercial silica sol which had been alkali stabilized to a molar ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of about 40 and which had particles with a specific surface area of 500 m^2/g .

Test No	Cationic starch	Polyacryl- amide	Polymeric silicic acid	Retention
	g/kg (kg/t)	g/kg (kg/t)	g/kg (kg/t)	%
1	-	-	-	20.0
2	8	-	-	35.3
3	-	0.3	-	36.9
4	8	0.3	-	57.6
5	8	-	0.5	78.0
6	8	-	1.0	85.3
7	-	0.3	1.0	40.7
8	8	0.3	0.5	82.1
9	8	0.3	0.75	96.2
10	8	0.3	1.0	93.5

In this case a considerably greater part of fine fibers and fillers are retained in the paper if all three components are used, in comparison with any of the other combinations. The tests with the commercial silica sol gave the following results:

Test No	Cationic starch	Polyacryl- amide	Silica sol 500 m ² /g	Retention
	g/kg (kg/t)	g/kg (kg/t)	g/kg (kg/t)	%
11	8	0.3	0.75	79.0
12	8	0.3	1.0	83.5

As evident the effect obtained with polymeric silicic acid of high specific surface area surpassed that obtained with the commercial sol.

Claims

1. A process for the production of paper from a suspension of cellulose containing fibers, and optional fillers, whereby cationic polymer and an anionic inorganic substance are added to the suspension and the suspension is formed and dewatered on a wire, characterized in that to the fiber suspension is added a cationic polyacrylamide, a cationic starch and a polymeric silicic acid having a specific surface area of at least 1050 m²/g.
2. A process according to claim 1, characterized in that the polymeric silicic acid has a specific surface area within the range of from 1100 to 1700 m²/g.
3. A process according to claim 1 or 2, characterized in that the polymeric silicic acid is such a polymeric silicic acid which has been prepared by acidification of an alkali metal water glass to a pH within the range of from 1.5 to 4.
4. A process according to claim 1, 2 or 3, characterized in that the polymeric silicic acid has been prepared by acidification by means of an acid cation exchanger.
5. A process according to any of the preceding claims, characterized in that the polymeric silicic acid is added in an amount of at least 0.01 g/kg (kg/t), calculated as SiO₂, on dry fibers and optional fillers.

6. A process according to claim 1, characterized in that the weight ratio of cationic starch and cationic polyacrylamide to polymeric silicic acid, calculated as SiO_2 , is above 0.1:1.
7. A process according to claim 1, characterized in that the weight ratio of cationic starch to cationic polyacrylamide is within the range of from 0.5:1 to 200:1.
8. A process according to claim 1, characterized in that the cationic starch is added to the fiber suspension before the cationic polyacrylamide and the polymeric silicic acid.
9. A process according to any of the preceding claims, characterized in that fiber content of the suspension comprises at least 25 per cent by weight of fibers from mechanical pulp and/or pulp from recycled fibers.

Patentansprüche

1. Verfahren zur Herstellung von Papier aus einer Cellulosefasern enthaltenden Suspension und gegebenenfalls Füllstoffen, wobei ein kationisches Polymer und eine anionische, anorganische Substanz zu der Suspension zugegeben werden und die Suspension auf einem Drahtnetz geformt und entwässert wird, dadurch gekennzeichnet, daß ein kationisches Polyacrylamid, eine kationische Stärke und eine Polykieselsäure mit einer spezifischen Oberfläche von mindestens $1050 \text{ m}^2/\text{g}$ zu der Fasersuspension zugegeben wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Polykieselsäure eine spezifische Oberfläche im Bereich von 1100 bis $1700 \text{ m}^2/\text{g}$ hat.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Polykieselsäure durch Ansäuern eines Alkalimetallwasserglases auf einen pH-Wert im Bereich von $1,5$ bis 4 hergestellt wurde.
4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß die Polykieselsäure durch Ansäuern unter Verwendung eines sauren Kationenaustauschers hergestellt wurde.
5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Polykieselsäure in einer Menge von mindestens $0,01 \text{ g/kg}$ (kg/t), berechnet als SiO_2 auf der Basis der trockenen Fasern, gegebenenfalls Füllmaterialien, zugefügt wird.
6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Gewichtsverhältnis der kationischen Stärke und des kationischen Polyacrylamids zu der Polykieselsäure, berechnet als SiO_2 größer als $0,1:1$ ist.
7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Gewichtsverhältnis der kationischen Stärke zu dem kationischen Polyacrylamid im Bereich von $0,5:1$ bis $200:1$ liegt.
8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die kationische Stärke vor dem kationischen Polyacrylamid und der Polykieselsäure zu der Fasersuspension zugefügt wird.
9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß der Fasergehalt der Suspension mindestens $25 \text{ Gew.}\%$ Fasern aus mechanischer Pulpe und/oder Pulpe von wiederverwerteten Fasern umfaßt.

Revendications

1. Procédé de production de papier à partir d'une suspension de fibres contenant de la cellulose, et de charges éventuelles, dans lequel on ajoute à la suspension un polymère cationique et une substance minérale anionique, et la suspension est mise en forme et épaissie sur une toile métallique, procédé caractérisé en ce que l'on ajoute à la suspension de fibres un polyacrylamide cationique, un amidon cationique et un acide silicique polymère qui présente une aire spécifique d'au moins $1050 \text{ m}^2/\text{g}$.
2. Procédé conforme à la revendication 1, caractérisé en ce que l'acide silicique polymère présente une aire spécifique située dans l'intervalle allant de 1100 à $1700 \text{ m}^2/\text{g}$.

3. Procédé conforme à la revendication 1 ou 2, caractérisé en ce que l'acide silicique polymère est un acide silicique polymère que l'on a préparé par acidification d'un verre soluble d'un métal alcalin à un pH situé dans l'intervalle allant de 1,5 à 4.
- 5 4. Procédé conforme à la revendication 1, 2 ou 3, caractérisé en ce que l'acide silicique polymère a été préparé par acidification au moyen d'un échangeur de cations sous forme acide.
5. Procédé conforme à l'une quelconque des revendications précédentes, caractérisé en ce que l'acide silicique polymère est ajouté à raison d'au moins 0,01 g/kg (kg/t), quantité calculée en SiO₂, par rapport aux fibres sèches et aux charges éventuelles.
- 10 6. Procédé conforme à la revendication 1, caractérisé en ce que le rapport pondéral de l'amidon cationique et du polyacrylamide cationique à l'acide silicique polymère, exprimé en SiO₂, vaut plus de 0,1/1.
- 15 7. Procédé conforme à la revendication 1, caractérisé en ce que le rapport pondéral de l'amidon cationique au polyacrylamide cationique se situe dans l'intervalle allant de 0,5/1 à 200/1.
8. Procédé conforme à la revendication 1, caractérisé en ce que l'amidon cationique est ajouté à la suspension de fibres avant le polyacrylamide cationique et l'acide silicique polymère.
- 20 9. Procédé conforme à l'une quelconque des revendications précédentes, caractérisé en ce que les fibres contenues dans la suspension comprennent au moins 25% en poids de fibres provenant d'une pâte mécanique et/ou d'une pâte de fibres recyclées.

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